



6th WORKSHOP

Green Chemistry and Nanotechnologies
in Polymer Chemistry



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Eds. - M. F. Barreiro, O. Ferreira, A.I. Pereira



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P51. VALORISATION OF ALMOND AGRO-INDUSTRIAL RESIDUES: PRODUCTION OF BIOPOLYOLS FROM ALMOND SHELL

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Introduction

The almond is a nut, well-known and quite produced in Portugal, especially in the region of Trás-os-Montes e Alto Douro and Algarve. Almond tree (*Prunus dulcis*) is a mid-size tree of the *Rosaceae* family (rose family). At global level almond production and processing generates millions of tons of residues in addition to almond nuts. Almond residues, including shells, hulls, pruning, leaves, skin and discharged inedible kernel, are viable feedstocks for a wide range of value-added products.

Almond fruit (Fig. 1) accounts with 80% (w/w) of residues (hull, shell and skin). Presently, the shell still finds use as energy source being commercialized by almond processing industries at a cost of 0.11 €/kg. Hulls are discharged during harvesting and skin can be obtained as a residue of the almond blanching process. Both of these residues have at present no economic value.



Fig. 1. Almond fruit residues: Hulls (A), Shell (B) and Skin (C).

Face to the present scenario of the almond cultivation and processing industry where residues can be easily recovered separately, the proposal of new applications over the traditional ones and of higher potential added-value, are motivating. Also, in a context where biomass conversion appears as an attractive and viable alternative to petroleum-based sources to produce chemicals, energy and materials, the study of these strategies can help to consolidate and promote the biorefinery concept.

In this context, this work aims at review the traditional uses of almond processing residues and to propose new ones in the field of chemicals and materials. A special focus will be put in the production of bio-polyols from the almond shell by means of oxypropylation processes.

Experimental

Background: The main scope of the oxypropylation process is to obtain polyols, in the form of viscous liquids, which can be interesting co-monomers to produce polyurethanes and polyesters [1]. Oxypropylation is a polymerization process that forms grafts of poly (propylene oxide), from available hydroxyls leading to the conversion of many intractable biomass residues into liquid polyols. Theoretically, any biomass residue containing hydroxyl groups can be transformed by oxypropylation into a liquid polyol (total oxypropylation) or into a biphasic polyol (partial oxypropylation). In general, each biomass residue needs to optimize reaction conditions and formulation in order to achieve the desired polyol properties face to a pre-determined application.

Oxypropylation reaction: The oxypropylation reaction was carried out in bulk using a pressure reactor of 450 mL. This reactor is equipped with a heating mantle, mechanical stirrer, thermocouple and manometer. It enables to work with temperatures ranging up to 350 °C and pressures up to 200 bar. To proceed with the oxypropylation reaction, the desired amounts of almond shell (AS), propylene oxide (PO) and the catalyst (KOH) were placed into the reactor that was thereafter closed and heated under stirring until a set point temperature of 160 °C. Usually no further processing is needed and the polyols proceed for characterization. Two AS/PO (w/v, g/ml) were tested (30/70 and 20/80) by using 3 catalyst contents (%_{wKOH/wAS}). For the sample 30/70, 2% KOH was also tried.

Characterization: The AS substrate was characterized in terms of lignocellulosic composition, lignin and ash contents. The obtained polyols were characterized in what concerns, homopolymer content (HOMO, %(w/w)), viscosity (20 °C, Pa.s) and hydroxyl number (IOH, mg_{KOH}/g).

Results and discussion

The AS substrate presented ash and moisture contents of 2.1% and 6.0%, respectively. In what concerns the lignocellulosic composition, 42.4% of holocellulose and 32.7% of lignin were determined. In a common oxypropylation experiment (Fig. 2), from an initial state, pressure and temperature start to increase progressively until a maximum value (P_{\max} and T_{\max}) which depended on the amount of catalyst and AS/PO ratio. After reaching P_{\max} , the pressure decreased rapidly reflecting the propylene oxide consumption. Table 1 reports the reaction conditions achieved for the performed oxypropylation assays. In a general way a time between 1 1.5 hours is enough to complete an oxypropylation reaction.

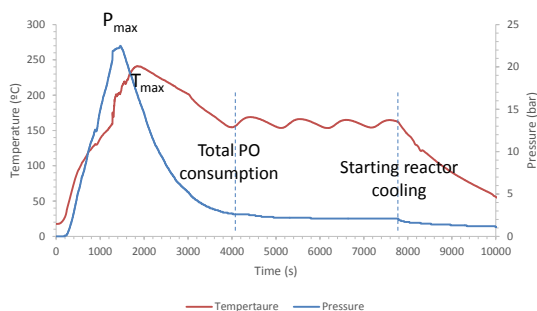


Fig. 2. Typical temperature and pressure profiles of an oxypropylation profile.

Table 1. Summary of the reaction conditions (T_{\max} , P_{\max} , and Time of T_{\max}) of the oxypropylation assays.

Formulation AS/PO/KOH (g/ml/%(w/w))	T_{\max} (°C)	P_{\max} (bar)	Time T_{\max} (min)
30/70/05	221	24.0	37
30/70/10	241	22.5	30
30/70/15	245	20.0	28
20/80/05	255	23.5	33
20/80/10	271	24.0	26
20/80/15	274	20.4	24

In a general way, and comparatively with other oxypropylation studies of the present research group dealing with other biomass substrates (e.g. lignin and olive stone) [1, 2], the obtained polyols are characterized by high IOHs (generally higher than 400). For the series 30/70 the content of unreacted substrate was around 10% (w/w) becoming lower for the series 20/80 (values lower than 2% were achieved). For very low catalyst contents (2%), very viscous polyols were obtained reason why this catalyst content was not attempted with the 20/80 AS/PO ratio. In a general way homopolymer content did not exceeded 10% for the series 30/70 being higher for the 20/80 ones.

Conclusions

Almond residues can be used for different purposes. Some of them are well established but others, even promising, are still under study. This is the case of the strategy presented in this work. Even preliminary, the results pointed out for the viability of using almond shell to produce biopolyols. This work under progress will continue by synthesizing the series 10/90, by completing the characterization and by testing the use of these biopolyols to produce rigid polyurethane foams. Other foreseen applications for almond agro-industrial residues include the recovery of bioactives from the almond skins and blanch water since they present significant amounts of phenolics and flavonoids (work under progress in cooperation with BioChemCore/CIMO-IPB). This recovery can be implemented at industrial level as a post-treatment of the blanch water proceeding from the blanching process.

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